

### **REMARKS**

Claims 1 and 6 have been amended to limit m based on recitations in claim 2 and the disclosure at page 6, line 10 to 12 in the patent specification. Claim 1 has also been amended to limit the glass temperature based on the disclosure at page 6, line 11 to page 7, line 2. Claim 2 has been canceled.

The specification has been amended to correct inadvertent errors in Tables 1 and 2. In particular, since some figures of "Ratio of isosorbide residue in all diol residues (wt%)" and "Ratio of isosorbide residue in all weight (wt%)" in Table 1 and 2 had been miscalculated, the former has been corrected and the latter has been deleted. The calculation procedure is shown as below and the corrected tables are attached in the end of this document. In addition, a correct expression of aliphatic alkylene glycol (pts.wt.) of example 17 in Table 2 is not "HD11.8 PD2.28" but "HD1.18 PD2.28".

#### **Ratio of isosorbide residue in all dial residues**

Considering example 1 of the application, the ratio of isosorbide in all diol residues is given as 97.8wt%. The diols used in this example are isosorbide and ethylene glycol, which are present in 29.23 parts by weight (abbreviated as pts.wt.) and 1.51 pts.wt., respectively. It would be self-evident to the skilled person, when using the formula outlined below, that the wt. % of isosorbide in all diol residues should not be as high as 97.8 wt%.

$$\text{Ratio of isosorbide residue in all residues} = \frac{\text{Isosorbide(pts.wt.)}}{\text{Isosorbide(pts.wt.)} + \text{aliphatic alkylene glycol(pts.wt.)}} \times 100$$

The above point is further exemplified when considering example 4 of the application, wherein the ratio of isosorbide in all dial residues is said to be 90.4wt%. The isosorbide and

ethylene glycol constituents in this example are present in 21.92 and 5.37 pts.wt., respectively. Accordingly, it would be self-evident to the skilled person that the ratio of isosorbide in all diol residues should be approximately 80wt% and not as high as 90.4wt%.

**Ratio of isosorbide residue in all weight**

The column of this ratio has been deleted in Table 1 and 2. The ratio was also incorrect, and the ratio did not have any meaning for this patent application.

Entry of the above amendment is respectfully requested.

**Art Rejection**

Claims 1-10 are rejected under 35 U.S.C. 102(b) as being anticipated by or, in the alternative, under 35 U.S. C. 103(a) over GB 1079686.

In response, Applicants note initially that Example 5 of GB 1079686 discloses a polycarbonate, which comprises isosorbide and diphenyl carbonate. The examiner has argued that this invention is anticipated, and the modification of the viscosity and the Tg is not unobvious but a routine method in the polycarbonate art.

Amended claim 1 requires the Tg to fall within the range from 100 to 160°C. Comparative example 1 noted by the Examiner bridging pages 2-3 of the Office Action, however, has a Tg of 163.7°C, which falls outside the scope of the amended claim.

As outlined at page 6 of the application (see the disclosure beginning at line 31) , the Tg is an important factor when considering the heat resistance of a molded product and its melt moldability. In order to retain these advantageous properties, it is preferred that Tg is within 100 to 160°C (see page 7, line 1 to 2).

If the skilled person had considered the disclosure in GB 1079686, it would not be apparent that a Tg between 100 and 160°C would be particularly advantageous when attempting to form a polycarbonate that has high heat resistance and melt moldability. Further, there is nothing in GB 1079686 to teach or suggest that adding additional diols, and in particular ethylene glycol, 1,3-propanediol and 1,6-hexanediol, to a polycarbonate would be particularly advantageous for its high heat resistance and melt moldability.

Further, Applicants note that the Canadian patent, CA 01170396 (which is an English language equivalent of EP 0025937 written in German) provides a discussion of the physical properties of the polycarbonate formed by example 5 of GB 1079686 (see page 2, line 11 to 28 of CA 01170396 attached). It is clear from the aforementioned passage in CA 01170396 that the polycarbonate of example 5 of GB 1079686 contains high melting, cross-linked constituents and, as a result, it exhibits such mediocre mechanical properties as to be broken up by manual pressure.

As mentioned above, keeping the Tg of the polycarbonate within 100 to 160°C is an important factor in retaining the heat resistance of a molded product and its melt moldability. The high melting, cross-linked constituents produced in the polycarbonate in example 5 of GB 1079686 would not give the advantageous properties conferred by the polycarbonates claimed in the present application (see also example 13 of the present application).

Moreover, there is no teaching or suggestion about the relationship between Tg and moldability in GB 1079686 and CA 01170396. Accordingly, if the skilled person had considered the teachings in GB 1079686 and the teachings in CA 01170396, they would not have been prompted to produce compounds that are structurally similar to those of the present application because they are said to give unfavorable properties.

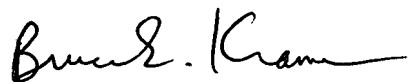
Thus, Applicants submit that the present invention is neither anticipated by nor obvious over GB 1079686, and withdrawal of this rejection is respectfully requested.

### Conclusion

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

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Table 1

	Isosorbide (pts. wt.)	Kind of aliphatic alkylene glycol	Aliphatic alkylene glycol (pts. wt.)	Diphenyl carbonate (pts. wt)	Isosorbide (mol%)	Aliphatic alkylene glycol (mol%)	Ratio of isosorbide residue in all diol residues (wt%)	Ratio of isosorbide residue in all weight (wt%)	Reduced viscosity	Glass transition temperature (°C)
Example 1	29.23	Ethylene glycol	1.51	49.48	89.3	10.7	97.8 <u>95.1</u>	95.9	0.353	157.4
Example 2	29.23		3.18	55.48	79.7	20.3	95.5 <u>90.2</u>	93.6	0.241	154.1
Example 3	21.92		3.87	46.91	63.5	36.5	93.1 <u>85.0</u>	91.1	0.191	130.1
Example 4	21.92		5.37	52.7	70.8	29.2	90.4 <u>80.3</u>	88.5	0.149	117.2
Example 5	14.61		6.08	41.99	50	50	70.3 <u>70.6</u>	68.4	0.128	107.3
Example 6	23.38	1,3-Propanediol	3.04	42.84	80	20	88.5	72.6	0.902	143.8
Example 7	26.31		1.52	42.84	90	10	94.5	78.3	0.298	150.7
Example 8	20.46		4.57	42.84	70	30	81.7	66.4	0.293	143.4
Example 9	26.3	1,4-Butanediol	1.8	42.84	90	10	93.6	77.6	1.155	156.7
Example 10	23.38		3.6	42.84	80	20	86.6	71.4	0.775	138.0
Example 11	23.38	1,5-Pentanediol	4.17	42.84	80	20	84.8 <u>84.9</u>	70.1	1.115	126.7
Example 12	20.46		6.25	42.84	70	30	76.5 <u>76.6</u>	62.9	0.585	90.4

Table 2

	Isosorbide (pts. wt.)	Kind of aliphatic alkylene glycol	Aliphatic alkylene glycol (pts. wt.)	Diphenyl carbonate (pts. wt)	Isosorbide (mol%)	Aliphatic alkylene glycol (mol%)	Ratio of isosorbide residue in all diol residues (wt%)	Ratio of isosorbide residue in all weight (wt%)	Reduced viscosity	Glass transition temperature (°C)
Example 13	26.31	1,6-Hexanediol	2.36	42.84	90	10	<u>91.7</u> <u>91.8</u>	<u>76.3</u>	0.932	145.2
Example 14	24.84		3.55	42.84	85	15	<u>87.4</u> <u>87.5</u>	<u>72.7</u>	0.704	131.2
Example 15	23.38		4.73	42.84	80	20	<u>83.0</u> <u>83.2</u>	<u>68.9</u>	1.139	122.6
Example 16	20.46		7.09	42.84	70	30	<u>74.1</u> <u>74.3</u>	<u>61.3</u>	1.168	95.6
Example 17	23.38	Two kinds of Diols (see notes)	HD1.18 PD2.28	42.84	80	HD5 PD15	<u>87.0</u> <u>87.1</u>	<u>71.7</u>	1.055	139.4
Example 18	23.38		HD2.36 PD1.52	42.84	80	HD10 PD10	<u>85.7</u> <u>85.8</u>	<u>70.7</u>	0.986	131
Example 19	20.46		HD2.36 PD3.04	42.84	70	HD10 PD20	<u>76.5</u> <u>79.1</u>	<u>64.6</u>	0.825	109.4
Example 20	20.46		HD3.55 PD2.28	42.84	70	HD15 PD15	<u>77.7</u> <u>77.8</u>	<u>63.8</u>	1.026	108.6
Example 21	20.46		HD4.73 PD1.52	42.84	70	HD20 PD10	<u>79.0</u> <u>76.6</u>	<u>62.9</u>	0.914	101.7
Example 22	23.38		HD2.36 BD1.80	42.84	80	HD10 BD10	<u>84.8</u> <u>84.9</u>	<u>70.1</u>	0.921	129.2
Example 23	24.84		BD1.80 EG1.24	44.99	85	BD10 EG5	<u>92.1</u> <u>89.1</u>	<u>75.9</u>	0.556	149.9
Comparative Example 1	29.23		—	44.13	—	—	100.0	<u>83.5</u>	0.457	163.7
Comparative Example 2	14.61	1,3-Propanediol	7.61	44.99	50	50	<u>65.7</u> <u>65.8</u>	<u>52.2</u>	0.166	63.3
Comparative example 3	14.61	1,4-Butanediol	9.01	44.99	50	50	<u>61.7</u> <u>61.9</u>	<u>49.6</u>	0.104	(Not measurable)
Comparative example 4	17.54	1,6-Hexanediol	9.45	42.84	60	40	<u>64.7</u> <u>65.0</u>	<u>53.4</u>	1.193	71.2

(Notes): EG—Ethylene glycol, PD—1, 3—Propanediol, BD—1, 4—butanediol, PeD—1, 5—Pentanediol, HD—1, 6—Hexanediol

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(19) (CA) **CANADIAN PATENT** (12)

(54) THERMOPLASTIC POLYCARBONATES, THEIR PREPARATION  
AND THEIR USE AS SHAPED ARTICLES AND FILMS

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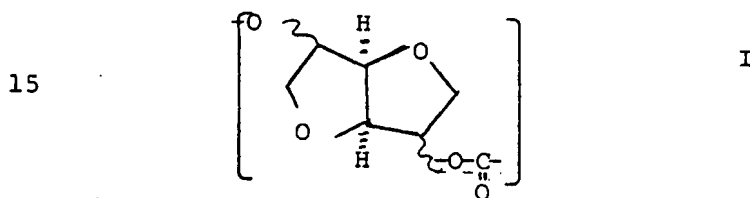
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THERMOPLASTIC POLYCARBONATES, THEIR PREPARATION  
AND THEIR USE AS SHAPED ARTICLES AND FILMSFIELD OF THE INVENTION

5 The invention relates to polycarbonates and to a method for their preparation.

BRIEF DESCRIPTION OF THE INVENTION

The present invention relates to high molecular weight thermoplastic polycarbonates which contain 0.1-50 mol %, preferably 5-50 mol % and in particular 10 20-50 mol %, relative to the total amount of carbonate structural units in the polycarbonate molecule of carbonate structural units from hexahydro-furo (3,2-b) furane-3,6-diols of the formula I



mixtures of two or more of the polycarbonates according to the invention and mixtures of the polycarbonates according to the invention with other thermoplastics, in particular with other polycarbonates based on diphenols.

20 DESCRIPTION OF THE PRIOR ART

Polycarbonates obtained from diphenols are old in the art. Possessing a combination of valuable properties, they have become very important materials for industrial and technological uses.

25 In contrast, polycarbonates obtained from aliphatic diols could hitherto find no application as structural materials. The reasons for this are the lower stability to heat and a certain difficulty in building up the high molecular weights associated with good mechanical 30 properties. Aliphatic polycarbonates have therefore been used industrially only as oligomers, for example as diol components in polyurethane chemistry.



extent of 50-99.9 mol %, in each case relative to the total molar amount of organic dihydroxy compounds employed, are tough, transparent, thermally stable thermoplastics having a general pattern of properties as good as that of the known aromatic polycarbonates.

DETAILED DESCRIPTION OF THE INVENTION

A process known for the preparation of polycarbonates is the melt transesterification method. In order to obtain high molecular polycarbonates by the melt transesterification method, as far as possible, equimolar amounts of OH equivalents resulting from diols and diphenols and of aryl carbonate or alkyl carbonate equivalents resulting from the particular sources of carbonate employed must be used and the final temperatures of the transesterification reaction must be over 300°C. However, if heterocyclic diols of the formula II are also used, branching occurs with the necessary residence times under these conditions, CO<sub>2</sub> being given off, and inhomogeneous products are thereby formed. The melt transesterification method is thus not very suitable for the preparation of the copolycarbonates according to the invention.

A preferred process for the preparation of aromatic polycarbonates is the phase boundary process (see for example, H. Schnell, Chemistry and Physics of Polycarbonates Interscience Publishers, 1964, pages 33 et seq., pages 9-14). In this process, one or more bisphenols in an aqueous alkaline solution are mixed thoroughly, with intensive stirring, with inert solvents, such as, for example, chlorinated hydrocarbons, and are converted into high molecular polycarbonates by introducing phosgene. However, if heterocyclic diols of the formula II are also used, no high molecular polycarbonates are obtained. The reason for this is the different reactivities of the aromatic bisphenols and heterocyclic diols. The method of phase boundary phosgenation is therefore unsuitable for the preparation of the polycarbonates according to the invention.

It has now been found that the copolycarbonates according to the invention can be prepared by the phase boundary process if the bis-halogenocarbonic acid esters of the furane-3,6-diols II are reacted with aromatic  
5 diphenols. If a proportion of diphenols of more than 50 mol %, relative to the total molar amount of dihydroxy compounds employed, is desired, phosgene or  $\text{COBr}_2$  must also be used.

The present invention thus also relates to a process  
10 for the preparation of the polycarbonates according to the invention containing 0.1 to 50 mol %, relative to the total amount of carbonate structural units in the polycarbonate molecule, of carbonate structural units of the formula I, which is characterized in that 0.1  
15 to 50 mol %, preferably 5 to 50 mol % and in particular 20 to 50 mol %, relative to the total molar amount of diphenols and bis-halogenocarbonic acid esters of the diols II, of diols of the formula II, in the form of their bis-halogenocarbonic acid esters, are reacted  
20 with 50 to 99.9 mol %, preferably 50 to 95 mol % and in particular, 50 to 80 mol %, relative to the total amount of diphenols and bis-halogenocarbonic acid esters of the diols II, of diphenols, if appropriate in the presence of chain stoppers and if appropriate  
25 also using phosgene or  $\text{COBr}_2$ , at temperatures between about 0 and about 80°C, preferably between about 10 and about 30°C, by the phase boundary process.

Bis-chlorocarbonic acid esters are particularly suitable bis-halogenocarbonic acid esters.

30 Examples of solvents which are suitable for the organic phase of the phase boundary process are halogenated aliphatics or halogenated aromatics, such as  $\text{CH}_2\text{Cl}_2$ , 1,2-dichloroethane, chlorobenzene, chlorobutanes and the like. NaOH, KOH or LiOH, preferably  
35 NaOH, is used to prepare the alkaline aqueous phase, the pH value during the reaction being between 9 and 14.

Catalysts which can be used for the polycondensation are tertiary aliphatic amines, for example, those with 3 to 20 C atoms, such as triethylamine, tri-n-propylamine, tri-n-butylamine, dimethyl-benzylamine and the like, 5 quaternary aliphatic ammonium salts, for example, those with 4 to 30 C atoms, such as tetramethyl-ammonium bromide, tetraethylammonium bromide, tetramethyl-ammonium chloride, tetraethylammonium chloride, trimethyl-benzylammonium chloride, trimethyl-n-butyl- 10 ammonium chloride, tetra-n-butyl-ammonium chloride and the like, and quaternary phosphonium salts and quaternary ammonium salts.

Phenols, such as, for example, phenol itself, alkyl-phenols, such as cresols or tert.-butylphenols, in 15 particular, p-tert.-butylphenol and halogenophenols, such as p-bromophenol, p-chlorophenol, 2,4,6-tribromophenol and 2,4,6-trichlorophenol function as chain stoppers in the customary manner. The chain stoppers are used in amounts of between 0.1 and 6 mol %, relative 20 to the number of mols of diphenols and bis-halogenocarbonic acid esters of the diols of formula II employed, depending on the desired molecular weight of the polycarbonates.

The reaction time can be between a few minutes and 25 some hours and the reaction has in general ended after 1 to 2 hours.

The amount of  $\text{COCl}_2$  or  $\text{COBr}_2$ , which can optimally also be used, is a function of the particular ratio of OH end groups and halogenocarbonic acid ester end groups 30 in the starting compounds, and an excess of about 10 mol % to about 50 mol %, preferably of about 10 mol % to about 30 mol %, is used in each case.

When the reaction has ended, the organic phase, containing the polycarbonate, is washed with water and 35 concentrated. The products can be isolated by precipitating the polycarbonates with a non-solvent, such as, for example, acetone, methanol or petroleum ether.

However, the concentrated polycarbonate solutions are preferably transferred to an evaporator extruder and extruded in a known manner. The yields of polycarbonate according to the invention are virtually  
5 quantitative.

Another process for the preparation of the polycarbonates according to the invention consists of reacting the bis-chlorocarbonic acid esters of the furane-3,6-diols of formula II with aromatic diphenols  
10 in a homogeneous solution.

In this process, the aromatic dihydroxy compounds to be employed and, if appropriate, chain limiters are dissolved in one of the organic solvents mentioned above for the phase boundary process, such as, for  
15 example,  $\text{CH}_2\text{Cl}_2$  or chlorobenzene, an equivalent amount of a tertiary organic base, such as, for example, N, N-dimethylaniline, dimethylcyclohexylamine or, preferably, pyridine, being added, and are reacted with corresponding amounts of bis-halogenocarbonic acid esters of the diols  
20 of formula II. If a proportion of diphenols of more than 50 mol %, relative to the total molar amount of dihydroxy compounds employed, is desired, phosgene or  $\text{COBr}_2$  must also be used.

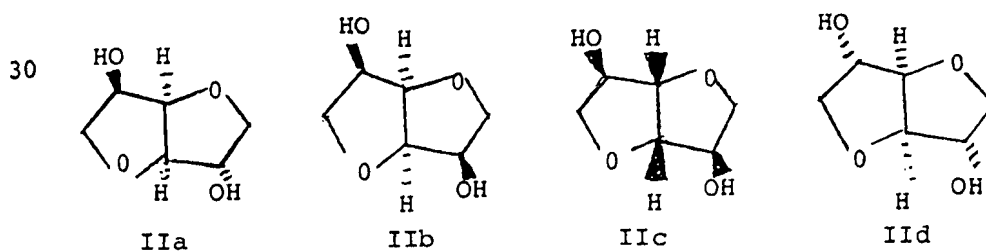
The reaction temperatures are between  $-10$  and  $+120^\circ\text{C}$   
25 and the reaction times are about half an hour to 12 hours. The polycarbonate solutions are worked up by a procedure in which the precipitated salt of the organic base is separated off by filtration or dissolved by adding a solvent, such as water. The organic phase, containing  
30 the polycarbonate, is washed with water and concentrated. The products can be isolated in the same manner as described above for the phase boundary process.

The present invention thus also relates to a process for the preparation of the polycarbonates according to  
35 the invention, which is characterized in that 0.1 to 50 mol %, preferably 5-50 mol % and in particular 20-50 mol %, relative to the total molar amounts of diphenols

and bis-halogenocarbonic acid esters of the diols of formula II, of diols of the formula II, in the form of their bis-halogenocarbonic acid esters, are reacted with 50-99.9 mol %, preferably 50-95 mol %, and in particular 50-80 mol %, relative to the total molar amount of diphenols and bis-halogenocarbonic acid esters of the diols of formula II, of diphenols, if appropriate in the presence of chain stoppers and if appropriate also using phosgene or  $\text{COBr}_2$ , in a homogeneous solution, with the addition of at least equivalent amounts of tertiary organic bases, preferably pyridine.

The bis-chlorocarbonic acid esters are particularly suitable bis-halogenocarbonic acid esters. The amount of phosgene to be employed in each case is between 0 and 150 mol %, relative to the diphenols and bis-halogenocarbonic acid esters of the diols of formula II. The reaction temperatures are between  $-10$  and  $+120^\circ\text{C}$ .

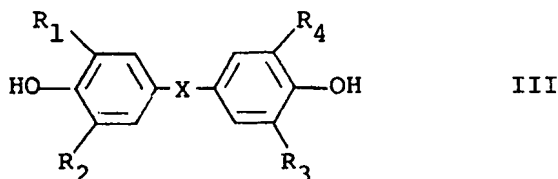
Diols of the formula II which are preferably employed for the polycarbonates according to the invention are (3aR)-(3aR,6ac)-hexahydro-furo-(3,2-b)-furane-3c,6t-diol, 1,4; 3,6-dianhydro-D-glucitol, IIa; (3aR)-(3aR,6ac)-hexahydro-furo (3,2-b)-furane-3t,6t-diol, 1,4; 3,6-dianhydro-D-mannitol, IIb; (3aS)-(3aR,6ac)-hexahydro-furo-(3,2-b)-furane-3c,6c-diol, 1,4; ~~3~~-dianhydro-D-iditol, IIc; and (3aR)-(3aR,6ac)-hexahydro-furo (3,2-b)-furane-3c,6c-diol, 1,4; 3,6-dianhydro-L-iditol, IId,



The diol of the formula IIa is particularly preferred according to the invention.

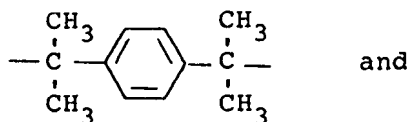
The diols which can be used according to the invention are known from literature and are prepared in a simple manner, usually from the corresponding hexitols by treatment with acids. Several methods for their preparation are reported in "Beilsteins Handbuch der Organischen Chemie" (Beilstein's Handbook of Organic Chemistry), 3rd and 4th supplement, volume 19/2, page 989 et seq.

In principle, any diphenols are suitable for the preparation of the polycarbonates according to the invention, and those of the following formula III



wherein

X denotes C<sub>1</sub>-C<sub>6</sub>-alkylene, C<sub>2</sub>-C<sub>6</sub>-alkylidene, C<sub>6</sub>-C<sub>10</sub>-cycloalkylene, C<sub>6</sub>-C<sub>10</sub>-cycloalkylidene, -CH-aryl, such as  $\text{CH}-\text{C}_6\text{H}_5$ , -C(aryl)<sub>2</sub>, such as -C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, -C-, -S-, -S(=O)-, -SO<sub>2</sub>-, -O-, a direct bond or



R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> independently denote H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, O-CH<sub>3</sub>, Cl or Br, are preferred.

Examples of diphenols which are suitable according to the invention are hydroquinone, resorcinol, dihydroxydiphenyls, bis-(hydroxyphenyl)-alkane, bis-(hydroxyphenyl)-cycloalkanes, bis-(hydroxyphenyl)-sulphides, bis-(hydroxyphenyl) ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl) sulfoxides, bis-(hydroxyphenyl) sulphones and α,α'-bis-(hydroxyphenyl)-diisopropylbenzenes, and nuclear-alkylated and nuclear

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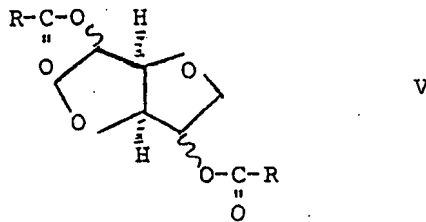


-C-A-O is the radical of the diphenol employed.

Copolycarbonates which are preferred according to the invention are those which are obtained from the preferred furane-3,6-diols IIa to IID and one or more of the preferred diphenols of the formula III.

5 Particularly preferred copolycarbonates are those which are obtained from 1,4; 3,6-dianhydro-D-glucitol and 2,2-bis-(4-hydroxyphenyl)-propane.

The bis-chlorocarbonic acid esters or bis-bromocarbonic acid esters of the diols II, of the formula  
10 V



wherein

R denotes Cl or Br,

which are suitable for the preparation of the polycarbonates according to the invention by the phase boundary process are new and can be obtained by known methods from the diols of the formula II with excess phosgene or  $\text{COBr}_2$ , preferably in the presence of inert bases, such as, for example, tertiary aliphatic amines or tertiary aliphatic-aromatic amines, such as, for example, triethylamine or dimethylaniline, and if appropriate in the presence of an inert organic solvent, such as, for example, aliphatic halogenated hydrocarbons, such as  $\text{CH}_2\text{Cl}_2$  or 1,2-dichloroethane.  
25 The reaction solution is worked up by a procedure in which the residual phosgene or  $\text{COBr}_2$  is decomposed by adding water, the amines are removed by washing the mixture with water containing hydrochloric acid, the mixture is then washed with distilled water and the organic phase is dried. The bis-chlorocarbonic acid esters and bis-bromocarbonic acid esters which  
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are suitable according to the invention can then be isolated in a pure form in a known manner, for example, by vacuum distillation.

5 The polycarbonates according to the invention can be modified in a known manner by incorporating small amounts, preferably 0.05 to 2.0 mol %, in each case relative to the organic dihydroxy compounds employed, of branching agents.

10 Examples of suitable branching agents are compounds which are trifunctional or more than trifunctional such as, for example, those with 3 or more phenolic hydroxyl groups, or isatin bisphenols according to German Auslegeschrift 2,500,092 (LeA 16,142), such as, for example, 3,3-bis-(4-hydroxyphenyl)-2-oxo-2,  
15 3-dihydroindole or 3,3-bis-(4-hydroxy-3-methylphenyl)-2-oxo-2,3-dihydroindole.

The polycarbonates according to the invention should as a rule have mean weight-average molecular weights  $\bar{M}_w$  of 10,000 to over 200,000, preferably 20,000 to  
20 80,000, determined by measuring the relative viscosity in  $\text{CH}_2\text{Cl}_2$  at 25°C and at a concentration of 0.5 % by weight.

Heat stabilizers, UV light and oxidation which are customary in polycarbonate chemistry can be added to  
25 the polycarbonates according to the invention during or after their preparation. Mold release agents and flameproofing agents customary for polycarbonates can also be added.

30 The heterocyclic-aromatic copolycarbonates according to the invention are distinguished by their very good mechanical, thermal and dielectric properties, their resistance towards many chemical agents, their density and transparency. Their high heat stability and high glass transition temperature, which in some cases  
35 exceeds those of the known bisphenol A polycarbonate are of particular value. Thus, the glass transition

temperature of a copolycarbonate according to the invention of 50 mol % of bisphenol A and 50 mol % of 1,4; 3,6-dianhydro-D-glucitol IIa is 162°C, while that of a pure bisphenol A polycarbonate is only 151°C.

5 The glass transition temperatures are in each case determined at a rate of heating of 20° K/minute on samples with a solution viscosity of  $\eta_{rel}$  of 1.30.

The thermoplastic polycarbonates mentioned are used in particular as structural materials for various  
10 applications, such as, for example, machine components, automobile components, casings, containers and electrical components. They can be processed by general methods of shaping, for example injection molding, extrusion and compression molding. Furthermore,  
15 because of the good solubility of the polycarbonates in chlorinated hydrocarbons, for example methylene chloride, films which can be used either as electrical insulating films or as carrier films can be produced by the casting process.

20 Dyestuffs, pigments, fillers and organic and inorganic fibers, such as, for example, glass fibers, can also be incorporated in the polycarbonates according to the invention in the amounts customary for polycarbonates.

25 Other thermoplastics, such as, for example, ABS, thermoplastic polyesters and in particular, other thermoplastic polycarbonates based on diphenols, can also be admixed with the polycarbonates according to the invention in any desired amounts, preferably  
30 in amounts of up to about 50 % by weight, relative to the total weight of polycarbonates according to the invention and the other thermoplastics, in order to modify further the pattern of properties of the polycarbonates according to the invention.

EXAMPLESComparison Example 1

For this example, Example 5 of British Patent Specification 1,079,686 is repeated. 14.6 g (0.1 mol) of 1,4; 3,6-dianhydro-D-glucitol, IIa, and 21.4 g (0.1 mol) of diphenyl carbonate are melted at 220°C under N<sub>2</sub>. 18.8 g of phenol are distilled off and the mixture is then subsequently stirred for further 30 minutes under 1 mm Hg.

The resulting polycarbonate is pale brown and essentially transparent, but include dark brown portions and the polycarbonate can be broken up by manual pressure. The solution viscosity  $\eta_{rel}$  (0.5 g in 100 ml of CH<sub>2</sub>Cl<sub>2</sub> at 25°) is 1.186 (after separating off insoluble constituents).

Comparison Example 2

Comparison Example 1 is repeated except that 14.6 g (0.1 mol) of 1,4; 3,6-dianhydro-D-mannitol, IIb, is being reacted. After a few minutes, even before the theoretically calculated amount of phenol has been distilled off, a grey-brown mass which can no longer be melted without decomposition, separates out. The product is not transparent, is insoluble in most organic solvents and is exceptionally brittle.

Comparison Examples 1 and 2 thus show that homopolycarbonates of the furane-3,6-diols II are unsuitable as thermoplastic materials.

Comparison Example 3

20.0 g (0.5 mol) of NaOH, 22.8 g (0.1 mol) of bisphenol A and 14.6 g (0.1 mol) of 1,4; 3,6-dianhydro-D-glucitol are dissolved in 600 ml of water under N<sub>2</sub>. After adding 600 ml of CH<sub>2</sub>Cl<sub>2</sub>, 30 g (0.3 mol) of phosgene are passed into the mixture, while stirring intensively. The aqueous phase is free from bisphenolate. 3 ml of a 3 % strength triethylamine solution are added and the mixture is subsequently

stirred for 60 minutes. The organic phase is separated off, shaken with 100 ml of 5 % strength phosphoric acid and washed with distilled water until free from electrolyte. The solution is  
5 evaporated. 23 g of colorless polycarbonate with a  $n_{rel}$  of 1.19 are obtained. However, investigation by IR and NMR spectroscopy shows that the product is a pure bisphenol A polycarbonate.

Comparison Example 3 thus shows that copolycarbonates  
10 of the heterocyclic diols of formula II and aromatic bisphenols cannot be prepared by the two-phase boundary phosgenation process.

#### Example 1

Bis-chlorocarbonic acid ester of 1,4; 3,6-dianhydro-  
15 D-glucitol.

43.8 g (0.3 mol) of 1,4; 3,6-dianhydro-D-glucitol are initially introduced into the reaction vessel at 0°C as a suspension in 400 ml of methylene chloride. 89.5 g (0.9 mol) of phosgene are passed in. A solution  
20 of 76.2 g (0.63 mol) of dimethylaniline in 100 ml of methylene chloride is added dropwise at  $0 \pm 2^\circ\text{C}$  in the course of 30 minutes. The mixture is subsequently stirred at 25°C for 2 hours and excess phosgene is then decomposed by adding water. The mixture is washed  
25 with water containing hydrochloric acid and then several times with distilled water and dried. The methylene chloride is evaporated off and the residue is distilled under a high vacuum. 70 g (86.1 % yield) of a colorless oil with a boiling point of 134°C/0.8  
30 mm Hg are obtained. The oil solidifies to give colorless crystals having a melting point of 44°C.

Analysis: Cl actual: 25.9 %

Cl calculated: 26.2 %

#### Example 2

35 Bis-chlorocarbonic acid ester of 1,4; 3,6-dianhydro-D-mannitol.

Analysis: Cl actual: 26.3 %  
Cl calculated: 26.2 %

Copolycarbonate of 1,4; 3,6-dianhydro-D-glucitol and bisphenol A.

10 20.0 g (0.5 mol) of NaOH, 22.8 g (0.1 mol) of  
bisphenol A, 300 mg (0.002 mol) of p-tert.-butylphenol  
and 322 mg (0.001 mol) of tetrabutylammonium bromide  
are dissolved in 500 ml of water, under N<sub>2</sub>. After  
15 adding 500 ml of CH<sub>2</sub>Cl<sub>2</sub>, a solution of 27.1 g (0.1 mol)  
of the bis-chlorocarbonic acid ester of 1,4; 3,6-di-  
anhydro-D-glucitol in 100 ml of CH<sub>2</sub>Cl<sub>2</sub> is added dropwise  
at room temperature, while stirring vigorously. The  
mixture is subsequently stirred for 60 minutes. The  
organic phase is separated off, shaken with 100 ml of  
20 5 % strength phosphoric acid and then washed until  
free from electrolyte, by repeated shaking with  
distilled water. The solution is evaporated. 38 g of  
a colorless, clear polycarbonate with a  $n_{rel}$  of 1.301  
are obtained.

25 The glass transition temperature (T<sub>g</sub>) (determined  
with a differential thermoanalyzer at a rate of heating  
of 20° K/minute) is 162°C.

Copolycarbonate of 1,4; 3,6-dianhydro-D-mannitol  
30 and bisphenol A.

Example 3 is repeated except that 27.1 g (0.1 mol) of the bis-chlorocarbonic acid ester of 1,4; 3,6-dianhydro-D- mannitol is employed.

The resulting copolycarbonate is colorless and  
35 clear and has a  $n_{rel}$  of 1.284 and a glass transition  
temperature ( $T_g$ ) of 133°C.

Example 5

Copolycarbonate of 1,4; 3,6-dianhydro-D-glucitol and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

Example 3 is repeated except that 26.8 g (0.1 mol) of 1,1-bis-(4-hydroxyphenyl)-cyclohexane is employed. The resulting copolycarbonate is colorless and clear and has a  $\eta_{rel}$  of 1.265 and a glass transition temperature ( $T_g$ ) of 176°.

Example 6

Copolycarbonate of 1,4; 3,6-dianhydro-D-glucitol and 4,4'-dihydroxydiphenyl sulphide (bisphenol S).

Example 3 is repeated except that 21.8 g (0.1 mol) of 4,4'-dihydroxydiphenyl sulphide is employed. The resulting copolycarbonate is colorless and clear and has a  $\eta_{rel}$  of 1.259 and a glass transition temperature ( $T_g$ ) of 132°.

Example 7

Copolycarbonate of 1,4; 3,6-dianhydro-D-glucitol and bisphenol A.

3,000 g (75 mols) of NaOH, 3,192 g (14 mols) of bisphenol A and 42 g (0.28 mol) of p-tert.-butylphenol are dissolved in 40 l of  $H_2O$ . After adding 40 l of  $CH_2Cl_2$ , a solution of 271 g (1.0 mol) of the bis-chlorocarbonic acid ester of 1,4; 3,6-dianhydro-D-glucitol in 500 ml of  $CH_2Cl_2$  is added dropwise at 20°C, while stirring intensively. The mixture is subsequently stirred for 10 minutes. 1,980 g (20 mols) of phosgene are then introduced. The aqueous phase is free from bisphenolate. 15 g of triethylamine are added and the mixture is subsequently stirred for 60 minutes. The aqueous phase is separated off and the organic phase is acidified with 2 % strength phosphoric acid and then washed with distilled water until free from electrolyte. 7 kg of chlorobenzene are added. The solution is evaporated and transferred to a vacuum extruder. Extrusion at 270° gives 3.2 kg of clear, colorless granules having a  $\eta_{rel}$  of 1.315. A molar

ratio of bisphenol A: 1,4; 3,6-dianhydro-D-glucitol of 14:1 is established by NMR spectroscopy. The following values were determined by testing rods of this product:

5	Vicat B:	148°
	Impact strength:	Unbroken
	Notched impact strength:	36.9 kJ/m <sup>2</sup>
	Tensile strength:	56.3 MPa
10	Elongation at break:	84 %
	Yield stress:	65.1 MPa

Example 8

15 Copolycarbonate of 1,4; 3,6-dianhydro-D-glucitol and bisphenol A.

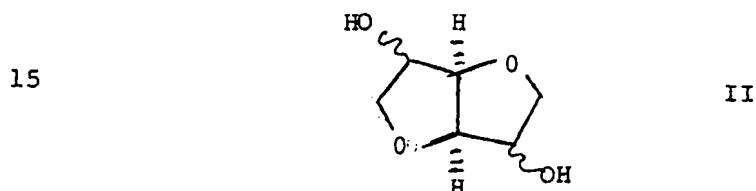
22.8 g (0.1 mol) of bisphenol A, 23.7 g (0.3 mol) of pyridine and 150 mg (0.001 mol) of p-tert.-butyl-phenol are dissolved in 400 ml of CH<sub>2</sub>Cl<sub>2</sub>, under N<sub>2</sub>. A solution of 27.1 g (0.1 mol) of the bis-chloro-

20 carbonic acid ester of 1,4; 3,6-dianhydro-D-glucitol in 100 ml of CH<sub>2</sub>Cl<sub>2</sub> is added dropwise at +2°C in the course of 30 minutes. The mixture is subsequently stirred at 0 to +5°C for 3 hours. After filtering, the organic phase is washed with dilute HCl, and then

25 with distilled water until freed from electrolyte. The solution is added dropwise to methanol. 36 g of a light polycarbonate powder having a  $\eta_{rel}$  of 1.231 are obtained.

Yet, it has always been of interest to the chemical industry to replace raw materials derived from limited natural resources by raw materials of vegetable origin, i.e. naturally occurring, which can be produced as desired. Thus, for example, the replacement of mineral oil and the diphenols obtainable therefrom by starch and the oligosaccharides, hexitols and the like which can be produced from starch is of economic interest. In contrast to diphenols, relatively large amounts of, for example, sorbitol, are available in this way.

It is known, from British Patent Specification 1,079,686, that high molecular polyesters and polycarbonates can be prepared from hexahydro-furo-(3,2-b)-furan-3,6-diols of the formula II.



which are preparable in a simple manner by dehydration of hexitols. However, these products, polyesters and in particular, polycarbonates, cannot yet be used industrially. The reason is their unsatisfactory properties profile. Although a high molecular weight polycarbonate of 1,4; 3,6-dianhydro-D-glucitol is indeed obtained according to Example 5 of British Patent Specification 1,079,686. It contains higher melting, cross-linked constituents and because of these inhomogeneties possess only mediocre mechanical properties. Use of 1,4; 3,6-dianhydro-D-mannitol in this process yields but pulverulent, crystalline compositions.

Surprisingly, it has now been found, in contrast, that heterocyclic aromatic copolycarbonates which are built up from heterocyclic diols of the formula II to the extent of 0.1-50 mol %, and from diphenols to the